

Spectrum of Gases Liberated upon the Stepwise Heating of Single-Walled Carbon Nanotubes Deuterated under Pressure

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The mass spectra of gases liberated from single-walled carbon nanotubes saturated with deuterium under a pressure of 5 GPa at temperatures up to 500°C (10.8 wt % D) have been measured at different steps of heating to 550°C in a vacuum. Hydrocarbons were found to dominate in the spectra at temperatures up to 400°C, whereas the D₂ and HD molecules became the main components of the spectra at 500–550°C. Changes in the spectra with temperature are consistent with the hypothesis that the major portion of hydrogen in the single-walled carbon nanotubes hydrogenated under pressure and reverted to normal conditions was present in the molecular form. The low temperatures of the hydrocarbon liberation are indicative of lower kinetic barriers in the reaction paths of the hydrocarbon liberation as compared with the liberation of D₂ molecules. Spectral-peak-shape analysis demonstrates the high hydrophilicity of hydrogenated single-walled carbon nanotubes, whereas the sorption of atmospheric oxygen is insignificant as compared with the sorption of water. © 2004 MAIK “Nauka/Interperiodica”.

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Previously [1], samples with a hydrogen content of 6.7–7.0 wt % H were prepared by the thermal treatment of single-walled carbon nanotubes and graphite nanofibers at 450°C and a hydrogen pressure of 9 GPa followed by liquid nitrogen quenching. The measurements of the pressure of a gas evolved into a closed volume on continuously heating the hydrogenated single-walled carbon nanotubes demonstrated that a small portion of the gas (0.45 wt % on a pure hydrogen basis) escaped from the sample at temperatures lower than ~50°C, whereas the liberation of the major portion of gaseous products began at about 500°C and reached a value of 5.6 wt % on a hydrogen basis at 650°C. According to elemental analysis data, after the hydrogenation of single-walled carbon nanotubes under pressure and reversion to normal conditions, the concentration of hydrogen was noticeably higher (6.8 wt % H). Therefore, it was assumed that a portion of the hydrogen could be released on heating as hydrocarbons with an atomic ratio of H/C > 2. The partially and fully degassed products were studied by IR spectroscopy and x-ray diffraction analysis [1]. It was found that covalent C–H bonds in nanostructures hydrogenated under pressure were responsible for the addition of no more than 40% of the absorbed hydrogen. The major portion of hydrogen occurred in the state that was inactive in IR spectra.

The aim of this work was to determine the composition of the gases evolved on heating hydrogenated single-walled carbon nanotubes by mass spectrometry. In

addition to information on the character of the gas evolution, these data allow us to reveal the state of the hydrogen in single-walled carbon nanotubes. In this study, we used a heavy isotope of hydrogen (deuterium) for the saturation of single-walled carbon nanotubes in order to decrease and, as far as possible, take into consideration the contribution of the ambient atmosphere and other experimental factors. In contrast to the previous work [1], we reduced the pressure of saturation with hydrogen to 5 GPa.

EXPERIMENTAL PROCEDURE

The carbon nanotubes were synthesized by an electric arc method using a nickel–yttrium catalyst. The primary condensation products containing 10–15 wt % single-walled carbon nanotubes were purified by repeated oxidation in air at temperatures up to 550°C alternated with washing in hydrochloric acid for the removal of amorphous carbon and the metal catalyst. According to microprobe analysis data, the metal impurities in the purified nanotubes were Ni and Y catalysts, as well as Cu and Zn, in the ratio Ni : Y : Cu : Zn = 1 : 1.5 : 0.6 : 0.7. The total metal concentration was no higher than 1 wt %. The incombustible residue upon the combustion of a weighed sample in oxygen was consistent with the total oxide amount to within ±30%. The structures of the condensation and purification products were studied previously using high-resolution electron microscopy, optical microscopy, and optical absorption

spectroscopy over the range 200–1400 nm [2, 3]. The sensitivity of the absorption spectra in the near-IR region to the purity of products [3, 4] was used for the quantitative determination of the amount of single-walled carbon nanotubes, which was equal to 80–85 wt % in the test samples of the given batch. According to the electron-microscopic data, graphitized black particles and graphite blocks up to 10–15 μm in size were the main impurities in the material and the nanotubes exhibited a narrow diameter distribution with an average value of 1.5 nm. The nanotubes occurred in the sample in a strongly aggregated state as strands, microcrystal films, and polycrystalline covers.

For the deuterium saturation, a 95-mg sample of single-walled carbon nanotubes and 130 mg of AID_3 (the source of the deuterium) were placed in a copper ampule and separated with a hydrogen-permeable membrane of palladium foil 0.02 mm in thickness. An anvil cell was used to produce a high pressure. The decomposition of the AID_3 was performed by heating the ampule to 350°C at a pressure of 1.5 GPa; then, the pressure was increased to the final value of 5 GPa. The single-walled carbon nanotubes were deuterated during a two-step exposure at $T = 350^\circ\text{C}$ for 21 h and then at $T = 460\text{--}490^\circ\text{C}$ for 9 h. Thereafter, the cell was cooled to room temperature and unloaded. The single-walled carbon nanotubes were loaded into and removed from a copper ampule in air; the samples were kept hermetically sealed during the rest of the time before the testing. The hydrogenation procedure was described in more detail in [5], where it was applied to the synthesis of C_{60} hydrofullerenes.

The composition of the deuterated samples was analyzed by the combustion of a weighed portion of 3 mg in a flow of oxygen at 1100°C followed by the gravimetric determination of the resulting CO_2 and D_2O . No correction for hydrogen impurity was made. According to the results of the two tests, the deuterated single-walled carbon nanotubes contained 10.8 ± 0.1 wt % D.

The mass spectra of the gases liberated from the test sample upon heating in a vacuum were measured with the use of an MI 1201V mass spectrometer. A 70-eV electron beam was used for the gas ionization in the ion source of the spectrometer. To obtain the gas phase, a weighed portion of the deuterated single-walled carbon nanotubes (about 80 mg) was placed in a quartz ampule of a pyrolyzer. This ampule was connected to the injection system of the mass spectrometer through a fine control valve. The quartz ampule with the sample was evacuated to a pressure of about 2×10^{-5} Pa in order to remove the surface and weakly bound impurities from the sample. After the evacuation, the ampule was isolated from the vacuum system and the sample was heated to 550°C in five steps. At each of the steps, the sample was kept at a fixed temperature for 3 h; next, the fine control valve was opened and the mass-spectrometric analysis of the gas collected in the ampule was performed. After the analysis, the quartz ampule was

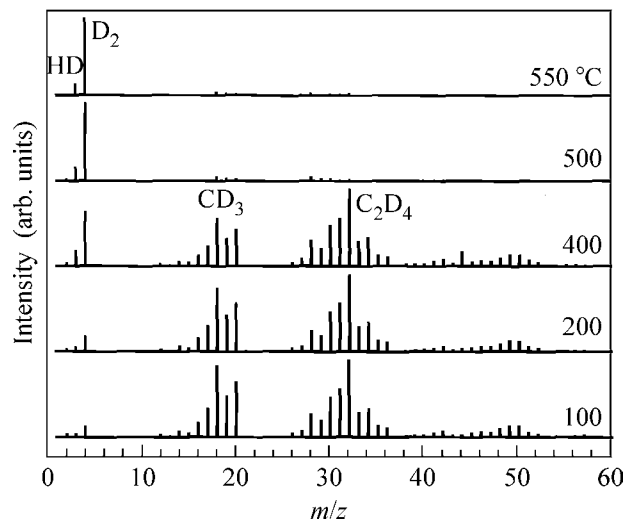


Fig. 1. Mass spectra of the gas phase over a sample of deuterated single-walled carbon nanotubes measured under stepwise heating to specified temperatures. The spectra are restricted to the value of $m/z = 60$, because the intensities of the peaks due to heavy ions are insignificant. The most intense peaks are identified tentatively (see the text).

again evacuated to a high vacuum, the valve was closed, and the sample was heated to the next temperature. The measurements were performed over the range $1 \leq m/z \leq 90$, where m is the atomic mass and z is the ion charge. The resolution of the spectrometer was approximately equal to 0.08%.

RESULTS AND DISCUSSION

Figure 1 shows the mass spectra of gases liberated at various steps during the heating of deuterated single-walled carbon nanotubes. A hydrocarbon mixture was the main constituent of the gas phase at temperatures to 400°C. Both deuterated hydrocarbons (as evidenced by the high intensities of the peaks with $m/z = 17\text{--}20$ and $31\text{--}36$) and compounds including the light isotope (because peaks with odd mass numbers were present in the spectra) were the constituents of this mixture. The former of these facts implies that the measured spectra describe the properties of the sample rather than the contributions of experimental factors. The latter fact is an indication that the impurities of the light hydrogen isotope or its compounds (which participated in the reactions in the course of the thermal treatment) were present in the parent single-walled carbon nanotubes or in the AID_3 source of the deuterium.

The presence of a minor impurity of protium in both the parent single-walled carbon nanotubes and AID_3 was found in special experiments. Because the AID_3 and the single-walled carbon nanotubes were separated by a Pd membrane in the course of the deuteration, the impurity of the protium or its compounds in the AID_3 (total concentration of about 2%) did not complicate

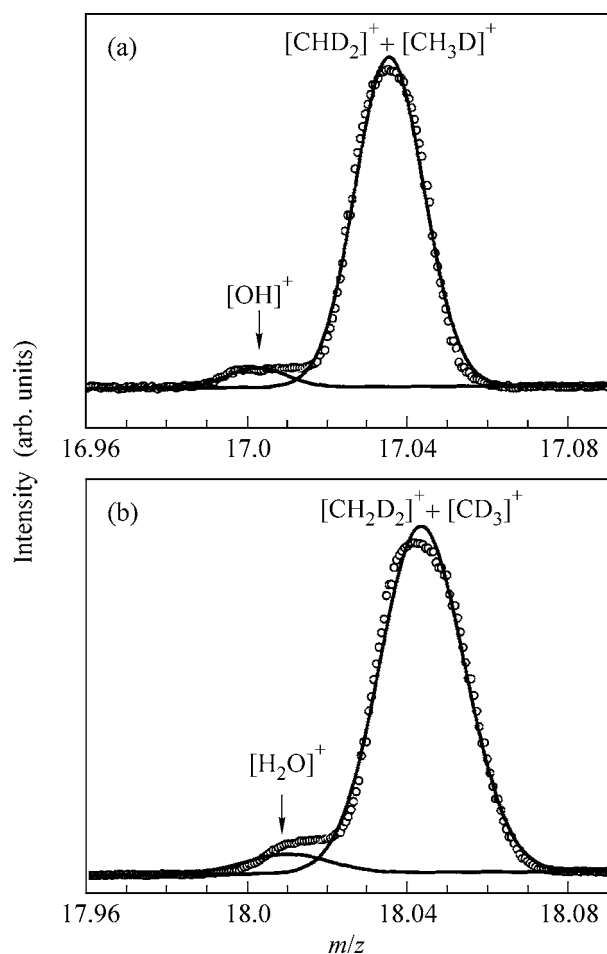


Fig. 2. Peak structures at $m/z =$ (a) 17 and (b) 18 in the mass spectrum measured upon heating to 100°C.

the interpretation of the spectra in this work. The solvents and gas atmospheres used at the stages of the preparation and purification could have been a source of impurities in the single-walled carbon nanotubes. A peak with $m/z = 31$ (corresponding to the $[\text{CH}_3\text{O}]^+$ ion) exhibited a maximum intensity in the spectrum of the parent single-walled carbon nanotubes; intense peaks with $m/z = 45, 59,$ and 74 were also detected. The origin of these peaks should be attributed to the fragmentation of diethyl ether. The presence of an acetone impurity also cannot be excluded. Both of the solvents were used at the stage of drying of the single-walled carbon nanotubes. At 200°C or higher, the peaks with $m/z = 44$ ($[\text{CO}_2]^+$) and 28 ($[\text{CO}]^+$) became most intense. In the spectra of deuterated single-walled carbon nanotubes in Fig. 1, the peaks with the above values of m/z exhibit low or zero intensities. Therefore, impurities of this type can be primarily considered as the source of protium.

The dramatic difference between the compositions of gas mixtures collected below 400°C and at higher temperatures is most pronounced in the spectra shown

in Fig. 1. The concentration of D_2 molecules in the gas phase increased as the temperature was increased from 100 to 400°C. In the spectra measured after heating to 500 and 550°C, the peaks with $m/z = 4$ and 3 were the most intense peaks. Consequently, D_2 and HD molecules were mainly present in the gas phase at these temperatures. This change in the shape of the spectra with the temperature is consistent with the previous hypothesis [1] that the major portion of the hydrogen was present in the molecular form in the single-walled carbon nanotubes hydrogenated under pressure. Indeed, based on thermodynamic data [6], we can calculate that the $0.47\text{CH}_4 : 0.53\text{H}_2$ atmosphere with a minor impurity of other hydrocarbons is an equilibrium atmosphere in the C–H system at $T = 500^\circ\text{C}$ and a pressure of about 0.1 MPa. If deuterium were attached to carbon fragments by covalent bonds in the samples, it would be expected that the fractions of deuteromethane and D_2 molecules in the high-temperature spectra would be comparable. We experimentally observed that the fraction of CD_4 decreased to almost zero at 500–550°C. This is indirect evidence for not only the absence of covalently bound deuterium but also the almost complete absence of the chemical etching of nanotube walls by deuterium.

Let us consider the structure of the spectra in more detail. Below 400°C, two groups of peaks with maximum group m/z ratios of 20 and 36, which correspond to deuteromethane and deuterioethane, respectively, can be recognized in the spectra. The peaks with $m/z > 52$ (deuteropropane) were insignificant in terms of their intensity. In the first group, two peaks ($m/z = 17$ and 18) exhibited a pronounced internal structure, which can be reliably interpreted.

The spectrum near $m/z = 17$ (Fig. 2a) is adequately described as a superposition of two Gaussian peaks centered at $m/z = 17.00275$ and 17.03598 , respectively. The more intense peak was due to $[\text{CHD}_2]^+$ ions with the tabulated value of $m/z = 17.03602913$ [7, 8] (henceforth, the tabulated values from [7] are italicized). The doubly charged ions $[\text{C}_2\text{D}_4\text{H}_2]^{2+}$ (*17.03602913*) and $[\text{C}_2\text{D}_5]^{2+}$ (*17.03525555*) can make small contributions as well. The smaller peak corresponds to $[\text{OH}]^+$ ions with the tabulated value of $m/z = 17.00274019$. The peak intensity of the $[\text{OH}]^+$ ion was about 5% of the base peak intensity. The following conclusion can be drawn from these data: Singly charged $[\text{CHD}_2]^+$ ions, which include both deuterium and protium, make the major contribution to the peak with $m/z = 17$, because the intensities of the peaks with $m/z = 17$ in Fig. 1 are similar to the intensities of the peaks with $m/z = 34$. The water content of the sample was very low (water was either initially present in the single-walled carbon nanotubes or trapped during manipulations with the sample in the open air). According to previously obtained data [1], the gas evolution upon heating from room temper-

ature to 400°C was no higher than 2% of the total gas evolution in the range to 550°C.

The spectra near $m/z = 18$ exhibited an analogous peak shape with a shoulder (Fig. 2b). Decomposition into Gaussians gave two peaks centered at $m/z = 18.0093$ and 18.04348 , respectively. We attributed the latter more intense peak in Fig. 2b to the ions $[\text{CD}_3]^+$ (18.04230666) and $[\text{CH}_2\text{D}_2]^+$ (18.04385482). Taking into account the intensity of the peak that was attributed above to $[\text{OH}]^+$ ions, we can explain the peak intensity at $m/z = 18.0093$ by the presence of only $[\text{H}_2\text{O}]^+$ ions (18.0105654). In this case, the contribution of $[\text{DO}]^+$ ions (18.00901722) can be disregarded even though the value of m/z is appropriate. This follows from the fact that the peak centered at $m/z = 20.05$ has no peculiarities, whereas the resolution of the spectrometer allowed us to reliably distinguish between peaks corresponding to the ions $[\text{CD}_4]^+$ (20.05640888) and $[\text{D}_2\text{O}]^+$ (20.02311946). Analogously, the peak with $m/z = 19$ has no peculiarities that could be associated with the presence of HDO molecules.

The above consideration of the peak structure excludes the participation of impurity water molecules in the process of the deuterium exchange in the course of the thermobaric treatment. In this case, the absorption of water by the deuterated sample from the atmosphere is the most likely mechanism of the appearance of an H_2O impurity. This fact is quantitative evidence for the hydrophilicity of hydrogenated carbon nanostructures.

We turn our attention to the most intense peak in spectra 1–3 (Fig. 1). This is the peak with $m/z = 32$. It would be expected that, in addition to hydrocarbon ions, such as $[\text{C}_2\text{D}_4]^+$ (32.05640888), $[\text{C}_2\text{D}_3\text{H}_2]^+$ (32.05795704), and $[\text{C}_2\text{D}_2\text{H}_4]^+$ (32.05950520), $[\text{O}_2]^+$ ions (31.98983004) also contribute to the intensity of this peak. The O_2 oxygen molecules, as well as water molecules, can be sorbed on the sample on contact with air. The spectrum profile near $m/z = 32$ shown in Fig. 3 appears as a single peak centered at $m/z = 32.0572$. The minor peculiarity at $m/z = 31.986$ (inset in Fig. 3) could be attributed to the presence of oxygen; however, its intensity is comparable to the background level and lower than 0.5% of the base peak intensity. Consequently, the sorption of oxygen molecules by deuterated single-walled carbon nanotubes from the atmosphere is less effective than the sorption of water.

The peaks due to hydrocarbons and their fragments (Fig. 1) exhibited higher intensities in all of the spectra at the steps of heating from 100 to 400°C, and the fraction of molecular deuterium in the gas phase became overwhelming only at 500°C. Deuterated hydrocarbons were likely formed at the stage of the saturation of single-walled carbon nanotubes with deuterium. They were retained by the sample during prolonged evacuation at room temperature; however, they were removed at lower temperatures as compared with the D_2 mole-

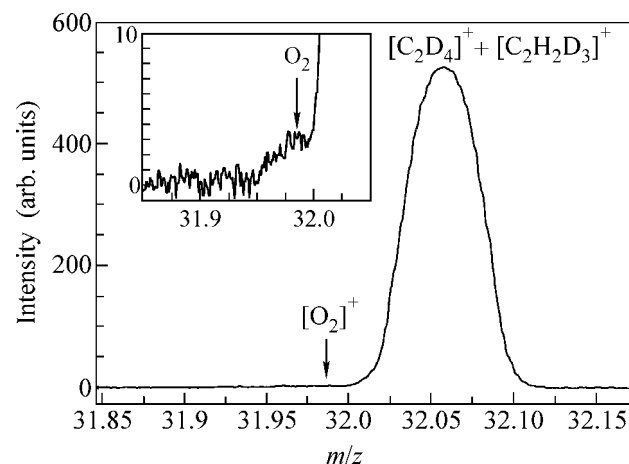


Fig. 3. Same as in Fig. 2 but at $m/z = 32$.

cules. Consequently, the kinetic barriers in the reaction paths of the hydrocarbon liberation should be lower than those for D_2 molecules. This suggests a difference in the positions of the hydrocarbon molecules and D_2 molecules in the structure of deuterated single-walled carbon nanotubes.

A comparison between the intensities of the peaks with even and odd mass numbers revealed one more property. The table, which summarizes the absolute and relative intensities of the peaks due to ions with $m/z = 1, 2, 3,$ and 4 , illustrates this property. It can be seen that the relative fraction of ions in which a deuterium atom is replaced by protium decreased as the temperature of the gas collection was increased. Similar changes with temperature can be observed by comparing the intensity ratios between the neighboring peaks of the hydrocarbons in the spectra corresponding to 100–400°C in Fig. 1. This property may be attributed to the greater mass of the D isotope and, correspondingly, to the longer time taken to diffuse from the sample rather than to the selectivity of single-walled carbon nanotubes for the absorption of isotopically different molecules.

Experimental peak intensities corresponding to deuterium and hydrogen ions. Values (%) normalized to the peak intensities of $[\text{D}_2]^+$ in the corresponding spectra are given in parentheses

$T, ^\circ\text{C}$	$m/z = 1$	$m/z = 2$	$m/z = 3$	$m/z = 4$
	$[\text{H}]^+$	$[\text{H}_2]^+, [\text{D}]^+$	$[\text{HD}]^+$	$[\text{D}_2]^+$
100	1.5 (2.1)	15.3 (21)	17.5 (24)	73.1 (100)
200	2.7 (1.6)	19.8 (12)	42.7 (26)	166.2 (100)
400	2.5 (0.5)	22.6 (5)	134.1 (27)	489.7 (100)
500	4.5 (0.2)	37.1 (2)	349.3 (17)	2056.6 (100)
550	3.4 (0.1)	43.1 (1)	667.2 (15)	4553.1 (100)

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